(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 013 585**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **80200017.4**

(22) Date of filing: **08.01.80**

(51) Int. Cl.³: **C 11 D 3/37**
C 11 D 1/83

(30) Priority: **12.01.79 US 2924**

(43) Date of publication of application:
23.07.80 Bulletin 80/15

(84) Designated Contracting States:
AT BE CH DE FR GB IT NL

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BE CH DE FR IT NL AT

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(54) **Light duty liquid detergent composition.**

(57) The present invention relates to a light duty, hand dishwashing, liquid composition comprising (a) an anionic surface active agent, a nonionic surface active agent, or mixtures thereof; (b) a copolymer of N-vinylpyrrolidone and dimethylamino-ethylmethacrylate having a molecular weight from about 40,000 to about 1,500,000, and (c) an alkali metal salt of casein. The compositions according to the invention possess drainage modification characteristics that produce rapid and uniform drainage of rinse water from washed utensils and apparatus without the disadvantage of spotting and filming.

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LIGHT DUTY LIQUID DETERGENT COMPOSITION

As liquid dishwashing detergent formulations become increasingly popular with the consumer, the performance of such detergent compositions for cleaning kitchen utensils, such as glasses, dishes and other apparatus, becomes more important. Many performance characteristics are associated with this type of detergent formulation, among which are foamability, detergency, soil suspending ability and mildness. In addition, the consumer has become concerned with both the final appearance of the objects that are washed and the ease with which washing, rinsing and the drying of the kitchen utensils can be accomplished.

Spotting may be referred to as resulting from the break-up of a once continuous liquid film followed by the isolation of liquid patches that become stranded on the solid surface. Upon the drying of these isolated liquid patches, spots will form from the solid residue that was dissolved or suspended in the liquid. One of the disadvantages associated with liquid dishwashing detergent compositions, therefore, is the need to dry the washed objects or apparatus with a towel so that spot and film formation from the minerals in the rinse water can be avoided or minimized to a large extent. Moreover, because of the amount of water that remains undrained on the glassware and plates and kitchen utensils, etc., the towel drying process tends to become time-consuming and an additional burden to the consumer, thereby leaving it more desirable to let the washed utensils or apparatus drain and dry by themselves under ambient conditions.

Various attempts have been made to minimize the effect of the water hardness residue and film-forming deposits on washed kitchen utensils by applying various additives in the detergent formulations, either by complexing the water hardness salts, or by formulating special rinsing agents. However, the incorporation of complexing and/or soil suspending agents in the liquid formulations create processing and formulation problems, while any of the special rinsing agents that have been disclosed heretofore must be packed and applied separately in the washing solution.

It has also been proposed to improve the drainage properties of dishwashing compositions by incorporating an agent, such as gelatin or casein, which allows the rinse water to "sheet-off" the utensil, thereby leaving the surface dry. This rapid "sheeting-off" effect reduces the effort involved in drying the washed objects and also improves their final appearance in terms of minimizing or altogether obviating the spotting and filming associated with suspended soil and water hardness.

Applicants have unexpectedly discovered that a liquid detergent composition containing a relatively small amount of a copolymer of N-vinylpyrrolidone and dimethylamino-ethylmethacrylate, having specific molecular weight limitations, and a small amount of an alkali metal salt of casein, e.g., sodium caseinate, when added to an anionic surfactant, nonionic surfactant, or mixtures thereof, provides an excellent washing and cleaning composition with much improved drainage properties so as to render the cleaned objects virtually free from spotting and/or filming.

The liquid detergent composition will generally contain from about 2% to about 50% by weight, preferably from about 10% to about 30% by weight of the total composition of an anionic surfactant compound.

Among the suitable synthetic anionic surface active agents that may be present in the liquid dishwashing detergent composition are the water-soluble hydrocarbon sulfates having the general

formula:

$$R_1O(C_2H_4O)_nSO_3M$$

wherein R_1 is a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 22 carbon atoms; n is from 0 to about 15; and M is a cation, preferably sodium, potassium or ammonium. Important examples which form part of the preferred composition of the present invention are the salts of an organic, sulfuric acid reaction product of a saturated or unsaturated fatty alcohol having 8 to 18 carbon atoms, preferably tallow or coconut alcohol, reacted with 1.5 to 15, preferably 3 to 13 moles of ethylene oxide per mole of fatty alcohol. Specific examples are C_{12-14} alkyl - O - $(C_2H_4O)_3$ - SO_3Na; C_{14} alkyl - O $(C_2H_4O)_3SO_3NH_4$; C_{12-16} alkyl - O - $(C_2H_4O)_6$ - SO_3K; and tallow - O - $(C_2H_4O)_9$ - $SO_3N(H)_2$ $(C_2H_4OH)_2$. Important examples of hydrocarbon sulfates as represented by the above formula whereby n is 0, are those obtained by sulfating hydroxylated hydrocarbons, preferably fatty alcohols having 8 to 18, most preferably 12 to 16 carbon atoms, with SO_3, H_2SO_4, etc. followed by hydrolysis and/or bleaching according to processes well known in the art.

Also suitable are the water-soluble salts of the organic sulfuric acid reaction products of the general formula:

$$R_2 - SO_3M$$

wherein R_2 is chosen from the group consisting of a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 24, preferably from 12 to 18 carbon atoms; and an alkylbenzene radical having from 8 to 18, preferably from 12 to 16 carbon atoms in the alkyl group; and M is a cation, preferably sodium, potassium, ammonium, magnesium or calcium. Important examples of the synthetic detergents which form a part of the preferred compositions of the present invention are the salts of an organic, sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, meso-, and n-paraffins, having 8 to

24 carbon atoms, preferably 11 to 18 carbon atoms, and 1 or 2 double bonds, and a sulfonating agent, e.g. SO_3, H_2SO_4, oleum, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are sulfonated C_{12-18} n-paraffins, alone or in combination with sulfonated alpha olefins containing an average of 14 carbon atoms. Important examples of alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 18 carbon atoms are dodecyl-, tetradecyl-, and hexadecylbenzene sulfonates and those which are described in U.S. Patents Nos. 2,220,099 and 2,477,383.

The preferred anionic surface-active agent which can be included in the composition of the present invention, is the water-soluble hydrocarbon sulfate as represented hereinbefore by the general formula $R_1O(C_2H_4O)_nSO_3M$, wherein R_1 is preferably a straight, saturated, aliphatic hydrocarbon radical, having from 8 to 20, desirably 12 to 16 carbon atoms; n is preferably from 3 to 9; and M is preferably sodium, potassium or ammonium. Said preferred ethoxylated hydrocarbon sulfates can be present in amounts up to 50%, but are preferably present between 5 and 35% by weight, based on the total weight of the composition.

In case of combinations of water-soluble, ethoxylated hydrocarbon sulfates, as represented by the aforementioned general formula $R_1O(C_2H_4O)_nSO_3M$, and water-soluble salts of the organic, sulfuric acid reaction product of the general formula R_2SO_3M, wherein R_1, R_2 and M and n have the same meaning recited above; the weight ratio of said water-soluble salts of the organic, sulfuric acid reaction product to the ethoxylated hydrocarbon sulfate will usually be, dependent upon the concentration and type of the metal cations present in the wash solution (i.e. the ionic strength), from about 10:1 to about 1:10, preferably from about 3:1 to about 1:1. The most preferred are those compositions whereby the water-soluble ethoxylated hydrocarbon sulfates are C_{12-16} alkyl - O - $(C_2H_4O)_{3-6}SO_3M$, and the water-soluble salts of the organic, sulfuric acid reaction products are C_{11-18} paraffin sulfonates.

The levels of nonionic surface-active detergent in the liquid detergent composition of the present invention will preferably be from about 1% to about 30% by weight, most preferably from about 1% to about 10% by weight based on the total weight of the composition.

Suitable, water-soluble, nonionic surface-active agents to be used in the formulation of the liquid dishwashing detergent composition of the present invention are the water-soluble, nonionic, tertiary amine oxides as represented hereinafter by the general formula:

$$R_3R_4R_5N - O$$

whereby R_3 represents a high molecular, straight or branched, saturated or unsaturated, aliphatic hydrocarbon, hydroxyhydrocarbon, or alkyloxyhydrocarbon radical, preferably an alkyl radical having a total of 8 to 24, preferably 12 to 18; R_4 and R_5 which may be the same or different, represent each a methyl, ethyl, hydroxymethyl, and hydroxyethyl radical.

They are generally prepared by direct oxidation of appropriate tertiary amines according to known methods. Specific examples of tertiary amine oxides are: dimethyl dodecyl amine oxide, diethyl tetradecyl amine oxide, bis-(2-hydroxyethyl)-dodecyl amine oxide, bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropyl amine oxide, dimethyl-2-hydroxydodecyl amine oxide, and diethyl eicosyl amine oxide.

Another group of suitable nonionic surfactant compounds are the water-soluble, tertiary phosphine oxides, represented by the general formula:

$$R_3R_4R_5P - O$$

whereby R_3, R_4 and R_5 have the same meaning as described hereinbefore. They can be prepared by alkylating an alkyl phosphine

derivative and oxidizing the resulting reaction product. Specific examples of tertiary phosphine oxides are: dimethyl dodecyl phosphine oxide, diethyl tetradecyl phosphine oxide, bis-(2-hydroxyethyl)- dodecyl phosphine oxide, tetradecyl ethyl 2-hydroxyethyl phosphine oxide, oleyl dimethyl phosphine oxide, and 2-hydroxydodecyl dimethyl phosphine oxide.

Still another group of nonionic surfactant compounds are the water-soluble amides represented by the general formula:

$$R_6 - CO - N(H)_{m-1}(R_7OH)_{3-m}$$

wherein R_6 is a saturated or unsaturated, aliphatic hydrocarbon radical having from 7 to 21, preferably from 11 to 17 carbon atoms; R_7 represents a methylene or ethylene group; and m is 1, 2 or 3, preferably 1. Specific examples of said amides are mono-ethanol coconut fatty acid amide, diethanol dodecyl fatty acid amide, and dimethanol oleyl amide.

Yet another group of nonionic surfactant compounds are the water-soluble condensation products obtained by condensing from 3 to about 25 moles of an alkylene oxide, preferably ethylene or propylene oxide, with one mole of an organic hydrophobic compound, aliphatic or alkyl aromatic in nature and having 8 to 24 carbon atoms and at least one reactive hydrogen atom, preferably a reactive hydroxyl, amino, amido or carboxy group. Specific examples of these groups of compounds are:

1. condensation products of ethylene oxide with aliphatic alcohols of more than 8 carbon atoms. The alcohols are usually derived from the naturally occurring fatty acids or from various branched-chain higher alcohols. Among the preferred alcohol-ethylene oxide condensation products are those made from alcohols derived from tallow and coconut fatty acids. Most preferred are the condensation products of about 4 to about 12 moles of ethylene oxide per mole of an aliphatic alcohol having from about 10 to about 18 carbon atoms, in particular a

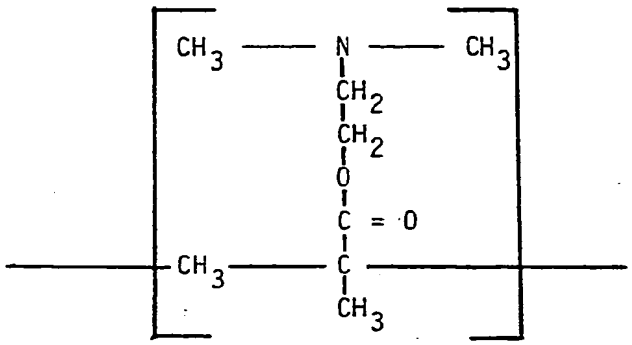
middle-cut coconut fatty alcohol condensed with 6 moles of ethylene oxide;

2. condensation products of ethylene oxide with alkylphenols, whereby the phenols may be mono- or polyalkylated and the total number of side-chain carbon atoms may be from 5 to 18 carbon atoms. The aromatic nucleus bearing the phenolic hydroxyl may be benzene, naphthalene, or diphenyl, preferably benzene. Specific examples are condensation products of one mole of nonylphenol with 9 to 15 moles of ethylene oxide;
3. condensation products of ethylene oxide with the fatty acid esters, preferably mono-fatty acid esters of the sugar alcohols, sorbitol and manitol, and also of di- and polysaccharides. Specific examples of the polyoxyethylene sorbitanmonolauric acid esters having 20 or more ethylene oxide units; and the polyoxyethylene derivatives of fatty acid partial esters of hexitol anhydrides generally known under the trade name TWEEN, available from ICI America, Inc., Wilmington, Delaware;
4. polyethenoxy esters, or esters formed by reacting ethylene oxide with carboxylic acids. The acids can be natural fatty acids or fatty acids made from oxidized paraffin wax, or mono- or alkylated benzoic and naphthenic acids. Desirable are aliphatic fatty acids having from 10 to 20 carbon atoms, and benzoic acids with 5 to 18 carbon atoms in the alkyl groups. Specific examples and preferred condensation products are tall oil ethylene oxide condensation products having 9 to 15 ethylene oxide units;
5. condensation products of fatty acyl alkanolamides of the type C_{7-17} alkyl - CO - NHC_2H_4OH, C_{7-17} alkyl - CO - N - $(C_2H_4OH)_2$ with ethylene oxide. Those preferred are condensation products of one mole of coconut - CO - NH - C_2H_4OH with 5 to 20 moles of ethylene oxide. Specific examples of polyethenoxy alkanolamides of fatty acids are the commercial products, marketed under the trade name ETHOMID, available from Armak Chemical Company, Chicago, Illinois;
6. condensation products of C_{8-18} alkyl-, C_{8-18} alkenyl- and C_{5-18} alkylaryl amines and ethylene oxide. A specific and preferred example is the condensation product of one mole of

dodecylamine with 9-12 moles of ethylene oxide.

The maximum level of water-soluble, anionic and nonionic surface-active agents that can be included in the liquid detergent composition of the present invention will usually depend on the level of each of the surfactants present and also to a certain extent on the presence of the drainage modification agents herein. The maximum amount of both nonionic and anionic surface-active agents which can be present in the composition of the present invention is about 50% by weight based on the total weight of the composition.

The copolymer used in the present liquid dishwashing detergent composition to provide enhanced drainage properties, is a copolymer of N-vinyl pyrrolidone and dimethylamino-ethylmethacrylate whose monomer structure is represented by the following formula:



The molecular weight of this copolymer is preferably between 40,000 and 1.5 million, and may be present in the composition from about 0.1% to about 10% by weight of the total composition, preferably between 0.5% and 3.0% by weight. A copolymer that is commercially available may be obtained from the GAF Corporation under the trade name of Gafquat 755, having a molecular weight of about 1 million, and Gafquat 734, having a molecular weight of about 100,000.

A third ingredient that is used in the dishwashing liquid composition of the invention is an alkali metal salt of the protein, casein, preferably sodium caseinate. The caseinate can be present in

an amount of from 0.5% to about 5% by weight based on the total weight of the composition, preferably from 1.0% to about 3.0% by weight. A commercial grade of sodium caseinate is available from Western Dairy Products under the trade name of Savortone LF having the following analysis:

	% Dry Weight
Protein	95
Fat	1.2
Ash	4.0
Moisture	4.0
pH (5% aqueous solution)	6.7

A more adequate description of casein and its salts may be found in the *"Fundaments of Dairy Chemistry"* by B.H.Webb, A.H.Johnson, and J.A.Alford, Avi Publication Co., Inc., 2d Ed. (1974), pp. 92-111, which is incorporated herein by reference.

Accordingly the invention pertains to a light duty, hand dishwashing liquid detergent composition comprising:

1. About 2% to about 50% by weight of an anionic surfactant compound, nonionic surfactant compound, or mixtures thereof;
2. About 0.1% to about 10% by weight of a copolymer of N-vinyl-pyrrolidone and dimethylamino-ethylmethacrylate having a molecular weight from about 40,000 to about 1,500,000; and
3. From 0.5% to about 5% by weight of an alkali metal salt of casein;

the percentages expressed being based on the total weight of the composition.

The above liquid detergent composition provides excellent drainage of washed kitchen utensils and apparatus, and prevents water spotting and filming when the utensils are left to dry. Moreover, the utensils are left with a shiny clean appearance and eliminate the necessity for towel drying or wiping.

A preferred embodiment for the dishwashing liquid detergent composition according to the invention is one which contains (a) from about 10 to about 50% of an anionic surfactant compound, or a mixture of anionic surfactant compounds; (b) from about 1% to about 10% of a nonionic surfactant compound, or a mixture of nonionic surfactant compounds; (c) from about 0.5% to about 3.0% of a copolymer of N-vinylpyrrolidone and dimethylamino-ethyl-methacrylate having a molecular weight between about 40,000 and 1.5 million, or mixtures thereof; and (d) from about 1.0% to about 3.0% of sodium caseinate; the percentages expressed being based on the total weight of the composition.

Additional ingredients that can be optionally included in the hand dishwashing liquid composition of the present invention are water-soluble, low molecular weight organic acid, or the water-soluble alkali metal, ammonium,or substituted ammonium salts thereof. Organic acids or their salts are added to enhance the cleaning action of the liquid detergent composition of the present invention and can, in addition, be used as a source of ions to maintain the pH of the composition at a given pH value. Suitable water-soluble, low molecular weight organic acids include, for example, acetic, citric, malic, gluconic, maleic, lactic, tartaric, propionic, butyric, malonic, polymaleic, polyitaconic, glutaric, citraconic, benzene pentacarboxylic, hexacarboxylic, succinic, ethylene diamine tetra-acetic and nitrilotriacetic acids. Partially and completely neutralized salts of the foregoing acids can also be used. Specific examples of suitable, organic acid salts are mono-, di- and trisodium citrate, diammonium citrate, monopotassium tartrate, disodium succinate, and tetrasodium melletate.

The maximum level of the water-soluble organic acids or salts that can be added to the liquid detergent composition of the present invention should usually not exceed 15 percent by weight of the total weight of the composition, and should preferably be below about 10 percent by weight. Some of the organic acid salts can be replaced by inorganic builder salts. The amount of inorganic builder salts, e.g. sodium phosphates and carbonates, should preferably not exceed

5 percent by weight in the composition.

Other suitable ingredients or additional compounds that can optionally be added to improve consumer acceptance of the composition of the present invention are: perfume, dyes, fluorescers, tarnish inhibitors, such as benzotriozole or ethylene thio-urea; shine improvers, such as boric acid or its salts in amounts of up to 3 percent by weight; bactericides such as 2-bromo-2-nitro-1, 3-propanediol, substituted benziodolium compounds, diphenyl ethers substituted with Cl, Br or $-CF_3$, e.g. 3,4-dichloro-4'-trifluoromethyldiphenyl ether; organic solvents, and hydrotropes;in amount of up to about 15 percent by weight to improve the pourability of the composition and to enhance the compatibility of the different components. Examples of the organic solvents are the mono- and dialcohols containing 2 to 8 carbon atoms such as ethanol, butanol, methylpropanol-1 and -2, amylol (pentanol), 1,2-,1,3- and 1,4-butanediol, toluol, benzyl carbinol, ethyleneglycol monobutyl ether, propyleneglycol propyl ether and diethyleneglycol dimethyl ether. Examples of hydrotropes are sodium,potassium or ammonium xylene sulfonate, and sodium, potassium or ammonium isethionate.

The benefits and advantages of the instant liquid dishwashing detergent composition are illustrated in the examples and tests set forth below.

Example 1

The substrates used to judge the effectiveness of the foregoing agents in the drainage modification in a liquid dishwashing detergent composition of all of the examples herein were either 310 ml drinking glasses, glass dinner plates (23 cm diameter), ceramic dinner plates (23 cm diameter), or plastic dinner plates (23 cm diameter), Boontonware. The substrates were washed with various detergent compositions at a use level of 0.15% and 0.20% for 1 minute and 3 minutes at a temperature of 40-45°C. Edgewater, New Jersey tap water was used in all of the experiments. The substrates were then rinsed either under running tap water or in a

dishpan filled with clean tap water. In both cases, the temperature of the rinse water was approximately 45°C. The duration of the rinse was varied between 10 seconds and 2 minutes.

After the rinse, the substrate was placed on a rack to dry. The time at which drainage began and the percentage of the surface area of the substrate that dried due to this drainage were recorded. The degree of benefit arising from the agent is directly related to the time at which drainage begins and the percentage of the area dried by this drainage. The benefit produced by drainage modification increases with increasing drainage rate and increasing percentage area dried by the enhanced drainage, provided that the rinse water film drains as a uniform sheet, and does not break up into water droplets which produce objectionable spotting.

The drainage agents used in the following tests are listed in Table 1 below.

Table 1

Drainage Modification Agent	Composition
PVP-K90*	Polyvinylpyrrolidone, MW ≅ 360,000
PVP-K30*	Polyvinylpyrrolidone, MW ≅ 40,000
Gafquat 755*	Copolymer of N-vinylpyrrolidone and dimethyl-amino-ethylmethacrylate, MW ≅ 1,000,000
Gafquat 734*	Copolymer of N-vinylpyrrolidone and methyl-amino-ethylmethacrylate, MW ≅ 100,000
Gelatin**	Type B, Bloom Strength 225
Savortone LF***	Sodium Caseinate

* Available from the GAF Corporation.

** Available from General Foods, Inc.; also described in USP 3,963,649.

*** Available from Western Dairy Products.

The influence of polyvinylpyrrolidone and the copolymer of N-vinyl-pyrrolidone and dimethylamino-ethylmethacrylate on the drainage of

rinse water from several substrates after washing with a liquid dishwashing composition is set forth in Table 3. The surfactant system used in these formulations is given in Tabel 2 below:

Table 2

Surfactant System	% by weight
Secondary alkane ($C_{15.3}$ avg.) sufonate (SAS-60)****	17
Ammonium C_{12}-C_{15} (3 ethylene oxide) sulfate	12
Lauryl diethanolamide	5
Ethanol	5
Water	to 100

**** Available from American Hoechst Corporation.

All of the results shown in Table 3 are compared with the base surfactant system given in Table 2 without the inclusion of a drainage modification agent.

Table 3

Effect of Drainage Modification Agents on Substrates

Agent	Concentration in Formulation	Time for Effect To Begin (seconds)			% Area Dried By Evaporation		
		Glasses	Glass Plates	Plastic Plates	Glasses	Glass Plates	Plastic Plates
No agent	--	--	--	--	100	100	100
PVP K-90	10%	9	--	--	<10	--	--
PVP K-90	5%	4	5	10	30	25	25
PVP K-90	2%	10	--	--	10-15	--	--
PVP K-90	1%	12	--	--	20	--	--
PVP K-30	10%	10	--	--	20-30	--	--
Gafquat-755	10%	8	--	--	10-20	--	--
Gafquat-734	10%	4	--	--	< 10	--	--
Gafquat-734	5%	3	3	10	< 10	10	25
Gafquat-734	2.5%	--	3	3	--	23	70
Gafquat-734	2.0%	10	--	--	15	--	--
Gafquat-734	1.0%	15	--	--	30	--	--
Gafquat-734	0.35%	12	--	--	50	--	--
Gafquat-734	0.21%	10	--	--	55	--	--
Na Caseinate	2.5%	12	3	4	70	75	76
Na Caseinate	2.0%	20	--	--	85	--	--
Na Caseinate	1.0%	--	--	--	100	--	--
Gelatin**	2.0%	10	--	--	85	--	--
Gelatin**	1.0%	12	--	--	85	--	--

Example 2

Mixtures of the copolymer of the present invention with sodium caseinate shows enhanced drainage modification on various substrates as compared with sodium caseinate used alone. This is demonstrated by the results shown in Table 4 with a surfactant system used according to Example 1.

Table 4

Drainage Modification Produced by Combination of Copolymer and Sodium Caseinate

Agent	Wt.% in Formulation	Ceramic Plates Time (sec.),	% Area	Plastic Plates Time (sec.),	% Area	Glass Plates Time (sec.),	% Area
Na Caseinate	2.5%	--	100	3	76	3	75
Gafquat-734	2.5%	4	40	3	70	3	23
Na-Caseinate -plus Gafquat-734	2.5% / 2.5%	2	2.5	3	73	2.5	1
Gafquat-734	5.0%	--	--	10	25	3	1

It will be seen that the sodium caseinate used alone is not as effective as when it is used in combination with the drainage modification agent according to the invention herein.

Example 3

The results described thus far in the foregoing tables have concerned the extent to which drainage modification agents according to the invention decrease the surface area that dries by evaporation for a given substrate, e.g. glassware. This rapid drainage not only facilitates the drying process but also significantly improves the final appearance of the glassware with respect to liquid dishwashing formulations. The following test illustrates the extent of this improvement in appearance.

Ten drinking glasses were soiled with milk. Five of the glasses were washed in a formulation containing 2.5% by weight of Gafquat-734 copolymer and 2.5% by weight of sodium caseinate in combination with the Surfactant Formulation described in Table 2. The remaining five glasses were washed in a solution of a commercial hand dishwashing liquid composition at an identical concentration of 0.20%. The commercial liquid composition is set forth below in Table 5. A panel of 12 people then compared the two sets of glasses with respect to spotting, filming and general appearance under normal laboratory lighting. The panel unanimously selected glasses washed in

the copolymer Gafquat-734/sodium caseinate formulation as having less spotting and filming and as having an overall "cleaner" appearance compared with glasses washed with the commercial product.

Table 5

Component	% by weight
Ammonium fatty (C_{12-14})alcohol (3 E.O.) sulfate	25.0
Potassium alkyl (C_{12-14}) oxyhydroxypropane sulfonate	3.8
Dimethyl alkyl amine oxide	6.0
Ethanol	5.6
Nonionic by-product (C_{12-14} fatty alcohol + C_{12-14} fatty alcohol (3 E.O.) ethoxylate)	2.5
KCl	2.5
NaCl	0.9
K_2SO_4	0.2
Water	to 100

Example 4

Samples of a surfactant system as used in Example 1 comprising the mixture according to the invention were compared with those containing only the copolymer or sodium caseinate alone.

The samples were examined on drinking glasses with respect to drain-dry performance and end result following rinsing. The washing tests were carried out at 42°C using precleaned glasses for each test at 0.2% product concentration under various water hardness conditions. Wash and rinse times were prolonged to optimise drain-dry effect; the treated glasses which had been rinsed were drained in an inverted position following the normal procedure.

The results are shown in the following Table 6.

TABLE 6

Effect of 2.5% Gafquat-734 and/or 2.5% sodium caseinate incorporated in base formulation

D.D. = Drain-dry

	6 - 6.5°H Water		11.4 - 12.3°H Water		18°H Water	
Agent	D.D. performance	End result	D.D. performance	End result	D.D. performance	End result
2.5% Gafquat-734 + 2.5% Na-caseinate	Unidirectionally D.D., wavy; tends to break from rim; acceptable	very good; negligible spotting	Unidirectionally D.D., slightly uneven; breaking slightly from rim later; acceptable	very good; negligible spotting	Unidirectionally D.D., slightly uneven; breaking slightly from rim; acceptable	good; some spots near rim
2.5% Gafquat-734	Multi-directionally D.D., leaving spots & trails; unacceptable	very good; negligible spotting	initially uni-directionally D.D., but later breaks all over from rim; unacceptable	fair; some considerable spotting near rim	unidirectionally D.D., slightly uneven inside; acceptable	fairly good; some spots & trails
2.5% Na-caseinate	mainly hydro-phylic; unacceptable	good; faint film; trace spots	mainly hydro-phylic; unacceptable	poor; extensive spotting and some film	slightly uneven and slightly slower on in-side, ther-wise OK	some spotting

The above results show that the composition of the invention is clearly superior in performance to the compositions outside the invention.

The results also indicate that there is a synergistic effect of sodium caseinate and Gafquat-734, a copolymer of N-vinylpyrrolidone and dimethylamino-ethylmethacrylate.

C L A I M S

1. A light duty, hand dishwashing, liquid detergent composition comprising

(a) from about 1% to about 50% by weight of an anionic surfactant compound, nonionic surfactant compound, or mixtures thereof;

(b) from about 0.1% to about 10% by weight of a copolymer of N-vinylpyrrolidone and dimethylamino-ethylmethacrylate having a molecular weight from about 40,000 to about 1,500,000, or mixtures thereof; and

(c) from 0.5% to about 5% by weight of an alkali metal salt of casein.

2. A liquid detergent composition according to claim 1 wherein component (c) is sodium caseinate.

3. A liquid detergent composition according to claim 1 wherein the anionic surfactant is a water-soluble hydrocarbon sulphate having the formula $R_1O(C_2H_4O)_nSO_3M$ wherein R_1 is a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 22 carbon atoms; n is an integer from 0 to about 15; and M is a cation of sodium, potassium or ammonium.

4. A liquid detergent composition according to claim 1 wherein the anionic surfactant is a compound of the formula

$$R_2 - SO_3M$$

wherein R_2 is a straight or branched, saturated or unsaturated, aliphatic hydrocarbon radical having from 8 to 24 carbon atoms, or an alkyl benzene radical having from 8 to 18 carbon atoms in the alkyl group; and M is a cation of sodium, potassium, ammonium, magnesium or calcium.

5. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a water-soluble tertiary amine oxide having the general formula $R_3R_4R_5N \rightarrow O$ wherein R_3 represents

a high molecular straight or branched, saturated or unsaturated, aliphatic hydrocarbon, hydroxyhydrocarbon, or alkyloxyhydrocarbon radical, having a total of 8 to 24 carbon atoms, and R_4 and R_5, which may be the same or different, represent each a methyl, ethyl, hydroxymethyl or hydroxyethyl radical.

6. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a compound of the formula

$$R_3R_4R_5P - O$$

wherein R_3 represents a high molecular, straight or branched, saturated or unsaturated, aliphatic hydrocarbon, hydroxyhydrocarbon, or alkyloxy hydrocarbon radical, having a total of from about 8 to about 24 carbon atoms; and R_4 and R_5, which may be the same or different, represent each a methyl, ethyl, hydroxymethyl or hydroxyethyl radical.

7. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a compound of the formula

$$R_6 - CO - N(H)_{m-1}(R_7OH)_{3-m}$$

wherein R_6 is a saturated or unsaturated, aliphatic hydrocarbon radical having from about 7 to about 21 carbon atoms; R_7 is a methylene or ethylene group; and m is an integer from 1 to 3.

8. A liquid detergent composition according to claim 7 wherein the nonionic surfactant is lauryl diethanolamide.

9. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a water-soluble condensation product of from about 3 to about 25 moles of an alkylene oxide and 1 mole of an organic, hydrophobic aliphatic or alkyl compound having at least one reactive hydrogen atom.

10. A liquid detergent composition according to claim 1 wherein the nonionic surfactant is a water-soluble condensation product of ethylene oxide with (a) an aliphatic alcohol having from about 10 to about 18 carbon atoms; (b) an alkylphenol;

(c) a fatty acid ester; (d) a polyethenoxy ester or an ester formed by reacting ethylene oxide with a carboxylic acid; (e) a fatty acyl alkanolamide; or (f) a C_8-C_{18} alkyl-, C_{8-18} alkenyl-, or C_{5-8} alkylaryl amine.

11. A liquid detergent composition according to claim 1, comprising:

(a) from about 10% to about 30% of an anionic surfactant compound, or a mixture of anionic surfactant compounds;

(b) from about 1% to about 10% of a nonionic surfactant compound, or a mixture of nonionic surfactant compounds;

(c) from about 0.5% to about 3.0% of a copolymer of N-vinylpyrrolidone and dimethylamino-ethylmethacrylate having a molecular weight between about 40,000 and 1.5 million; and

(d) from about 1.0% to about 3.0% of sodium caseinate;

the percentages expressed being based on the total weight of the composition.

0013585
Application number

European Patent Office

EUROPEAN SEARCH REPORT

EP 80 20 0017

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	DE - A1 - 2 607 656 (UNILEVER) * claim 1; page 6, paragraph 3; page 7, paragraph 2 * --	1,4, 5 9-11
	US - A - 4 048 301 (L'OREAL) * claims 1, 2 and 6; column 4, example A * --	1,8, 11
A	CH - A - 389 141 (COLGATE-PALMOLIVE) * complete document * --	
A	CH - A - 488 007 (HENKEL & CIE) * complete document * --	
A	US - A - 3 979 339 (PROCTER & GAMBLE) * complete document * ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 11 D 3/37
C 11 D 1/83

TECHNICAL FIELDS SEARCHED (Int.Cl.³)

C 11 D 1/00
C 11 D 3/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	11-04-1980	SCHULTZE

EPO Form 1503.1 06.78